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(54) **A NON-AQUEOUS ELECTROLYTE SYSTEM FOR USE IN BATTERIES, CAPACITORS OR
ELECTROCHROMIC DEVICES AND A METHOD FOR THE PREPARATION THEREOF**
NICHT-WÄSSRIGES ELEKTROLYTSYSTEM FÜR BATTERIEN, KONDENSATOREN ODER
ELEKTROCHROME ANORDNUNGEN UND DESSEN HERSTELLUNGSVERFAHREN
SYSTEME ELECTROLYTIQUE NON AQUEUX DESTINE A ETRE UTILISE DANS DES BATTERIES,
DES CONDENSATEURS OU DES DISPOSITIFS ELECTROCHIMIQUES ET SON PROCEDE DE
PREPARATION

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Description

[0001] This invention is related to a non-aqueous electrolyte system for use in batteries, capacitors or electrochromic devices, said system essentially consisting of an alkali or ammonium salt, a solvent mixture and optionally a polymer.

5 [0002] Liquid, solid and immobilized non-aqueous electrolytes are of considerable interest for use in lithium batteries, supercapacitors and other electrochemical devices.

10 [0003] Recently, lithium secondary batteries have been developed based on lithium insertion materials for both the negative electrode and the positive electrode. Such electrochemical cells have a cell voltage in excess of 4V in the charged state and an energy density of more than 100 Wh/kg. Similarly for the recently developed supercapacitor cells, voltages higher than 3V give considerable improvement with respect to the energy storage capability. However, electrolyte compositions used in these devices are traditionally limiting the device performance because of low ionic conductivity and low electrochemical stability. The demands for electrolytes in batteries and supercapacitors have been sufficiently fulfilled only with few organic carbonates or in particular with mixtures thereof.

15 [0004] US 5 192 629 of Bell Communication Research Inc. describes an electrolyte system comprising a solution of LiPF₆ in a mixture of dimethyl carbonate and ethylene carbonate.

20 [0005] EP 541 889 of Sanyo Electric Co. describes for lithium-ion graphite-based batteries the combination of a separator with a liquid electrolyte comprising one or more of the solvents ethylene carbonate, propylene carbonate, lactones and sulfolanes.

25 [0006] US 5 240 790 of Alliant Techsystems Inc. describes the use of a polyacrylonitrile-based gelled polymer system, which includes as an immobilised liquid phase a ternary plasticifier mixture of ethylene carbonate, γ -butyrolactone and polyethylene glycol dimethyl ether, in lithium-based electrode batteries.

30 [0007] US 5 326 657 of Nippon Oil Co. describes a polymeric solid ionic electrolyte having good mechanical properties. The polymeric solid electrolyte is a radiation crosslinked network based on a polyfunctional acrylate compound, containing a non-aqueous organic solvent and an alkali metal and/or an ammonium salt.

35 [0008] EP 651 455 of Matsushita Electrical Industrial Co Ltd. describes the use of a separator based on polyethylene and/or polypropylene to prevent lithium secondary batteries from shortcircuiting.

40 [0009] Although electrolyte systems showing high conductivity and which are stable against oxidation are known, there still exists a need for an electrolyte system which in addition to said high conductivity and high oxidation stability display a high stability against reduction.

45 [0010] Accordingly, it is an object of the invention to provide a non-aqueous electrolyte system for use in batteries, capacitors or electrochromic devices (including so-called "smart windows") which can be applied in a broad voltage range, which has a conductivity higher than 10⁻³ S/cm at room temperature, and which shows a high stability against reduction.

50 [0011] Now it has been found that this object is accomplished by an electrolyte system consisting essentially of an alkali or ammonium salt, a solvent mixture, and optionally a polymer, wherein said solvent mixture comprises at least 50 % by mole of a mixture of ethylene carbonate and γ -valerolactone, optionally containing one or more additional solvents selected from other organic carbonates, other lactones, esters and glymes, said system optionally being confined in a separator.

55 [0012] Whereas the pure γ -valerolactone is electrochemically stable against coke and graphite, the passivation layer formed upon reaction with the lithium containing negative electrode structures is poor, the lithium conductivity is poor, the reaction product is neither thermodynamically nor kinetically stable, and the cell balance is severely distorted as large amounts of active material is consumed in the passivation reaction.

60 [0013] In contrast, the ethylene carbonate displays good properties of the passivation layer formed, high conductivity, stability and low materials consumption. Pure ethylene carbonate, however, is solid at ambient temperature. Both of the materials γ -valerolactone and ethylene carbonate show good electrochemical stability vs. the cathode materials of lithium transition metal oxide type.

65 [0014] Surprisingly however, the mixture of γ -valerolactone and ethylene carbonate has been found to combine the preferred characteristics of the two individual components and furthermore results in high electrochemical stability against the negative electrode and formation of a high performance passivation layer.

70 [0015] Moreover, the highly conductive electrolyte system of the invention allows operation of rechargeable lithium batteries with cell voltages above 4V and supercapacitors with cell voltages above 3V.

75 [0016] Compared to the mixture of γ -butyrolactone and ethylene carbonate known from US 5 240 790, the mixture of ethylene carbonate and γ -valerolactone is a superior solvent mixture for high performance electrolyte applications, since said known and structurally close mixture displays poorer electrochemical stability against the negative electrode of the electrochemical system, although both mixtures shown an oxidation stability and conductivity which is non-restrictive for their application in the said electrochemical systems.

80 [0017] The improved stability towards reduction is mirrored in the cycling efficiency of the ethylene carbonate/ γ -valerolactone mixture, which is superior to the cycling efficiency of the ethylene carbonate/ γ -butyrolactone mixture. In

particular, a lower irreversible loss of active material is observed for the former mixture, the capacity of the electrochemical cell being sustained through a high number of cycles.

[0018] The ethylene carbonate and γ -valerolactone are preferably present in the solvent mixture in a relative molar ratio of from 20:80 to 80:20.

[0019] The solvent mixture is preferably composed of at least 90% of ethylene carbonate and γ -valerolactone.

[0020] In an even more preferred embodiment of the invention the solvent mixture of the electrolyte is composed essentially of ethylene carbonate and γ -valerolactone only.

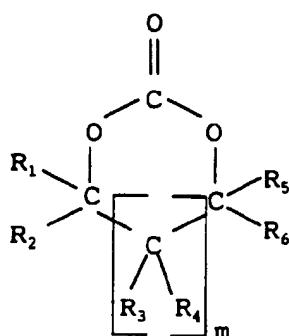
[0021] In an alternative embodiment of the invention the solvent mixture comprises, in addition to ethylene carbonate and γ -valerolactone, one or more of the following solvents:

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(a) alicyclic carbonates represented by the following general formula:

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wherein each of R₁, R₂, R₃, R₄, R₅ and R₆ independently represent hydrogen or C₁-C₂ alkyl groups and m is an integer equal to 0 or 1, with the proviso that when m is equal to 0, at least one of R₁, R₂, R₅ and R₆ is different from hydrogen, preferably propylene carbonate;

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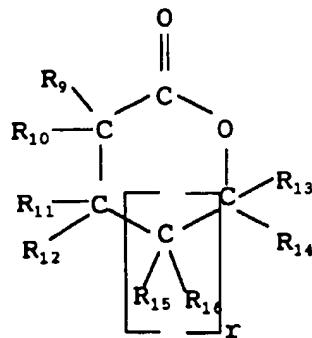
(b) aliphatic carbonates represented by the general formula R₇[OC(O)]_pOR₈, wherein R₇ and R₈ independently represent C₁-C₄ alkyl groups, and p is an integer equal to 1 or 2, preferably dimethyl carbonate and/or diethyl carbonate;

35

(c) lactones in the form of cyclic esters represented by the general formula:

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wherein each of R₉, R₁₀, R₁₁, R₁₂, R₁₃, R₁₄, R₁₅ and R₁₆ independently represent hydrogen or C₁-C₂ alkyl groups and r is an integer equal to 0 or 1, with the proviso that the value of r and the nature of the substituents are chosen so as to exclude γ -valerolactone from the definition, preferably γ -butyrolactone;

55

(d) esters represented by the formula R₁₇[C(O)]OR₁₈[OR₁₉]_t, wherein each of R₁₇, R₁₈ and R₁₉ independently represent hydrogen or C₁-C₂ alkyl groups, and t is an integer from 0 to 2, preferably an acetate, more preferably (2-methoxyethyl)-acetate and/or ethyl acetate;

(e) glymes represented by the general formula $R_{20}O(R_{21}O)_nR_{22}$, in which R_{20} and R_{22} independently represent C_{1-2} alkyl groups, R_{21} is $-(CR_{23}R_{24}CR_{25}R_{26})-$ wherein R_{23} , R_{24} , R_{25} and R_{26} independently each represent hydrogen or C_1-C_4 alkyl groups, and n is an integer from 2 to 6, preferably 3, R_{20} and R_{22} preferably being methyl groups, R_{23} , R_{24} , R_{25} and R_{26} preferably being hydrogen or C_1-C_2 alkyl groups, more preferably hydrogen.

5

[0022] Any salt commonly employed as an ion-conductive salt in batteries or capacitors may be used in the electrolyte system according to the invention. Preferably however, the salt is an alkali salt or a quaternary ammonium salt of ClO_4^- , $CF_3SO_3^-$, AsF_6^- , PF_6^- or BF_4^- , or any mixture of such alkali or ammonium salts, more preferably $LiAsF_6$, $LiPF_6$, $N(Et)_4PF_6$ or $N(Bu)_4PF_6$ or any mixtures thereof.

10 [0023] In order to provide mechanical integrity of the electrolyte, the electrolyte system preferably comprises a crosslinked or non-crosslinked, advantageously non-crosslinked, polymer produced by UV or heat induced polymerisation of monomers or oligomers containing one or more polymerisable functional groups, said polymer more preferably being a non-crosslinkable polyester, polyurethane, polyether or polyacrylate.

15 [0024] The polymer is preferably produced by heat induced polymerisation at a temperature lower than $70^\circ C$, performed on an electrolyte precursor containing electrolyte salt, solvent mixture and the above-mentioned monomers or oligomers.

20 [0025] The electrolyte system according to the invention is preferably incorporated in a separator consisting of a porous structure made from a polymer, preferably polyethylene, polypropylene, polycarbonate or cellulose. The separator acts as a matrix which confines the physical dimensions of the electrolyte system, thereby enabling the production of thin, self-sustaining and uniform electrolyte membranes. The separator is preferably a woven or non-woven structure having a pore size in the range of 10×10 nm to 1×1 mm and a thickness of $10-100\mu m$, preferably $10-25\mu m$. More specifically, the size of the pores can be as in a microporous film (e.g. a Celgard separator) or up to 1×1 mm as in a woven net having a mesh of this size.

25 [0026] The alkali or ammonium salt is preferably present in a concentration from 0.01M to 2.5M, more preferably 0.1M to 1.5M, in the electrolyte system. The polymer is preferably present in an amount corresponding to from 3% to 95% by weight, preferably 5% to 70% by weight, more preferably 5% to 40% by weight, even more preferably 15% to 40% by weight, relative to the total weight of the electrolyte system.

30 [0027] The present invention is furthermore concerned with a simple and economically advantageous method of the preparation of the electrolyte system of the invention, said method comprising mixing the solvents, dissolving the alkali or ammonium salts in the solvent mixture, optionally adding a thickening agent to the solution, and optionally adding monomers or oligomers containing one or more polymerisable functional groups, addition of a UV-photoinitiator or a heat-initiator, optionally incorporation of the obtained mixture in a separator and UV or heat curing of the monomers or oligomers.

35 [0028] In the following table I, some physical data of the ethylene carbonate and γ -valerolactone are listed.

TABLE I

Compound	Type	Nominal formula	melting point ($^\circ C$)	boiling point ($^\circ C$)
ethylene carbonate	alicyclic carbonate	$C_3H_4O_3$	38	243
γ -valerolactone	cyclic ester	$C_5H_8O_2$	-31	207

40 [0029] In the following examples preparation of various embodiments of the non-aqueous electrolyte system of the invention and the manufacture of various electrochemical devices containing the said electrolyte system is illustrated.

45 EXAMPLE I

50 [0030] A 1 M solution of $LiPF_6$ in ethylene carbonate/ γ -valerolactone (1:1 by weight) was prepared by dissolving 13.5 g of $LiPF_6$ in a mixture of 50 g of ethylene carbonate and 50 g of γ -valerolactone. The conductivity was measured by ac impedance spectroscopy at 65 kHz in an experimental cell with stainless steel electrodes. The conductivity was 8.2 mS/cm at $25^\circ C$. The electrochemical stability range of the electrolyte was measured by cyclic voltammetry at 200 mV/s in the range of 1-6 V vs. Li/Li^+ , using a Pt-microelectrode having a radius of 5 μm . The oxidation potential was defined as the potential at which the current exceeded 3 mA/cm², and was found to be 4.7 V vs. Li/Li^+ . The reduction behaviour was investigated applying the electrolyte in cells with Li-intercalating carbon-based negative electrode structures according to example III.

55

EXAMPLE II

5 [0031] To a 1M solution of LiPF₆ in a 1:1 mixture mixture of ethylene carbonate and γ -valerolactone was added 17.3% by weight of polyethylene glycol diacrylate (M.W:508) and 3% by weight of PEO (M.W: 600k). Subsequently, 3% by weight of polymerisation initiator (Darocure 1173) was added. The resulting UV-cured electrolyte had a conductivity of 2×10^{-3} S/cm at 20°C.

EXAMPLE III

10 [0032] A rechargeable Li/carbon cell was prepared by laminating together a 25 μ m thick lithium foil with 100 μ m of the electrolyte of example 1 and a 40 μ m thick carbon electrode. The carbon electrode was prepared by pressing a mixture of petroleum coke and binder onto a copper foil. The reversible capacity of the resulting cell was 200 mAh/g of carbon, and the irreversible loss was 50 mAh/g of carbon. The resistance of the cell was constant for more than 100 cycles, 75% of the initial electrode capacity being available after 100 cycles.

15 COMPARATIVE EXAMPLE A

20 [0033] A rechargeable Li/carbon cell was prepared in the same manner as described in example III, except from using γ -butyrolactone in stead of γ -valerolactone. The reversible capacity of the resulting cell was 170 mAh/g, and the irreversible loss was 60 mAh/g. The resistance of the cell increased significantly during the first 10 cycles, 75% of the initial electrode capacity being available after 10 cycles.

EXAMPLE IV

25 [0034] A lithium ion cell having a graphite negative electrode, a lithium manganese oxide positive electrode and an electrolyte system consisting of 1M LiPF₆ in a mixture of ethylene carbonate and γ -valerolactone was prepared. The resulting cell showed full utilisation of the positive electrode capacity. The cell was cycled between 3.2V and 4.2V and displayed 85% of the original capacity after 40 cycles.

30 EXAMPLE V

35 [0035] A 1M solution of N(Et)₄PF₆ in ethylene carbonate/ γ -valerolactone (1:1 by weight) was prepared by dissolving 27.5 g of N(Et)₄PF₆ in 50 g of ethylene carbonate and 50 g of γ -valerolactone. The conductivity was 12.4 mS/cm at 25°C. A capacitor was prepared from two carbon-based polymer-bound laminates, between which the electrolyte system was sandwiched. The resulting capacitor was cycled between 2.4V and 3.6V for more than 5000 cycles with a constant current of 1.0 mA/cm².

EXAMPLE VI

40 [0036] To a mixture of 4 g of ethylene carbonate and 3 g of γ -valerolactone was added 1.1 g of LiCF₃SO₃, 12.8 g of polyethylene glycol diacrylate (MW:508) and 4 g of 2-(2-ethoxyethoxy)ethyl acrylate. 1.6% of a photoinitiator (Darocure 1173) was incorporated in the mixture. This mixture was sandwiched between a WO₃ glass electrode and a counter glass electrode, applying an electrolyte thickness of 1 mm, and subsequently UV cured for 60 s. The resulting smart window was charged, say bleached, and discharged, say colored, for more than 1000 cycles.

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Claims

50 1. A non-aqueous electrolyte system for use in batteries, capacitors or electrochromic displays, said system consisting essentially of:

- an alkali or ammonium salt
- a solvent mixture, and optionally
- a polymer,

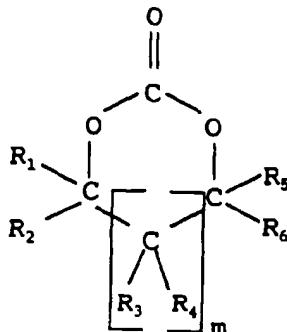
55 characterised in that the solvent mixture comprises at least 50 % by mole of a mixture of ethylene carbonate and γ -valerolactone, optionally containing one or more additional solvents selected from other organic carbonates, other lactones, esters and glymes, said system optionally being confined in a separator.

2. An electrolyte system according to claim 1, in which ethylene carbonate and γ -valerolactone are present in the solvent mixture in a relative molar ratio of from 20:80 to 80:20.

5 3. An electrolyte system according to claim 1 or 2, in which the solvent mixture is composed of at least 90% of ethylene carbonate and γ -valerolactone, preferably composed essentially of ethylene carbonate and γ -valerolactone only.

10 4. An electrolyte system according to claim 1 or 2, in which in addition to ethylene carbonate and γ -valerolactone comprises one or more of the following solvents:

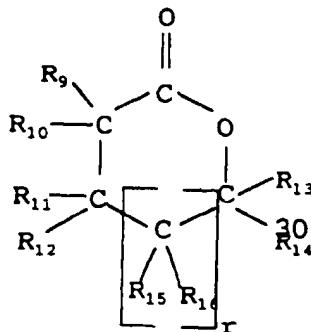
10 (a) alicyclic carbonates represented by the following general formula:



wherein each of R₁, R₂, R₃, R₄, R₅ and R₆ independently represent hydrogen or C₁-C₂ alkyl groups and m is an integer equal to 0 or 1, with the proviso that when m is equal to 0, at least one of R₁, R₂, R₅ and R₆ is different from hydrogen, preferably propylene carbonate;

30 (b) aliphatic carbonates represented by the general formula R₇[OC(O)]_pOR₈, wherein R₇ and R₈ independently represent C₁-C₄ alkyl groups, and p is an integer equal to 1 or 2, preferably dimethyl carbonate and/or diethyl carbonate;

35 (c) lactones in the form of cyclic esters represented by the general formula:



wherein each of R₉, R₁₀, R₁₁, R₁₂, R₁₃, R₁₄, R₁₅ and R₁₆ independently represent hydrogen or C₁-C₂ alkyl groups and r is an integer equal to 0 or 1, with the proviso that the value of r and the nature of the substituents are chosen so as to exclude γ -valerolactone from the definition, preferably γ -butyrolactone;

55 (d) esters represented by the formula R₁₇[C(O)]OR₁₈[OR₁₉]_t, wherein each of R₁₇, R₁₈ and R₁₉ independently represent hydrogen or C₁-C₂ alkyl groups, and t is an integer from 0 to 2, preferably an acetate, more preferably (2-methoxyethyl)-acetate and/or ethyl acetate;

(e) glymes represented by the general formula $R_{20}O(R_{21}O)_nR_{22}$, in which R_{20} and R_{22} independently represent C_{1-2} alkyl groups, R_{21} is $-(CR_{23}R_{24}CR_{25}R_{26})-$ wherein R_{23} , R_{24} , R_{25} and R_{26} independently each represent hydrogen or C_{1-4} alkyl groups, and n is an integer from 2 to 6, preferably 3, R_{20} and R_{22} preferably being methyl groups, R_{23} , R_{24} , R_{25} and R_{26} preferably being hydrogen or C_{1-2} alkyl groups, more preferably hydrogen.

5 5. An electrolyte system according any of the preceding claims, in which said salt is an alkali salt or a quaternary ammonium salt of ClO_4^- , $CF_3SO_3^-$, AsF_6^- , PF_6^- or BF_4^- , or any mixture of such alkali or ammonium salts, preferably $LiAsF_6$, $LiPF_6$, $N(Et)_4PF_6$ or $N(Bu)_4PF_6$ or any mixtures thereof.

10 6. An electrolyte system according to any of the preceding claims comprising a crosslinked or non-crosslinked, preferably non-crosslinked, polymer produced by UV or heat induced polymerisation of monomers or oligomers containing one or more polymerisable functional groups, said polymer more preferably being a non-cross-linkable polyester, polyurethane, polyether or polyacrylate.

15 7. An electrolyte system according to claim 6, in which the polymer is produced by heat induced polymerisation at a temperature lower than $70^\circ C$.

20 8. An electrolyte system according to any of the preceding claims, said system being confined in a separator consisting of a porous structure made from a polymer, preferably polyethylene, polypropylene, polycarbonate or cellulose.

9. An electrolyte system according to claim 8, in which said separator is in a woven or non-woven structure having a pore size in the range of $10 \times 10 \text{ nm}$ to $1 \times 1 \text{ mm}$.

25 10. An electrolyte system according to any of the claims 8 and 9, in which said separator has a thickness of $10-100 \mu\text{m}$, preferably $10-25 \mu\text{m}$.

11. An electrolyte system according to any of the preceding claims, in which the alkali or ammonium salt is present in a concentration from 0.01M to 2.5M , preferably 0.1M to 1.5M .

30 12. An electrolyte system according to any of the preceding claims, in which the polymer is present in an amount corresponding to from 3% to 95% by weight, preferably 5% to 70% by weight, more preferably 5% to 40% by weight, even more preferably 15% to 40% by weight, relative to the total weight of the electrolyte system.

35 13. A method for the preparation of an electrolyte system according to each of the preceding claims, comprising mixing the solvents, dissolving the alkali or ammonium salts in the solvent mixture and optionally adding a thickening agent to the solution.

40 14. A method according to claim 13 further comprising adding monomers or oligomers containing one or more polymerisable functional groups, addition of a UV-photoinitiator or a heat-initiator, optionally incorporation of the obtained mixture in a separator and UV or heat curing of the monomers or oligomers.

45 15. Use of an electrolyte system according to claims 1 to 12 in a battery, a capacitor and/or in an electrochromic display.

45 Patentansprüche

1. Nichtwässriges Elektrolytsystem für Batterien, Kondensatoren oder elektrochrome Displays, wobei das System im wesentlichen aus:

50 - einem Alkali- oder Ammoniumsalz
- einem Lösungsmittelgemisch, und gegebenenfalls
- einem Polymeren

55 besteht, dadurch gekennz Ichn t, daß das Lösungsmittelgemisch mindestens 50 mol% eines Gemisches aus Ethylenkarbonat und γ -Valerolacton umfaßt und daß es gegebenenfalls ein oder mehrere Lösungsmittel, ausgewählt aus anderen organischen Carbonaten, anderen Lactonen, Estern und Glymen, enthält, wobei das genannte System gegebenenfalls in einem Separator eingegrenzt ist.

2. Elektrolytsystem nach Anspruch 1, dadurch **gekennzeichnet**, daß das Ethylenkarbonat und γ -Valerolacton in dem Lösungsmittelgemisch in einem relativen Molverhältnis von 20:80 bis 80:20 vorhanden sind.

5 3. Elektrolytsystem nach Anspruch 1 oder 2, dadurch **gekennzeichnet**, daß das Lösungsmittelgemisch aus mindestens 90% Ethylenkarbonat und γ -Valerolacton besteht und daß es vorzugsweise im wesentlichen nur aus Ethylenkarbonat und γ -Valerolacton besteht.

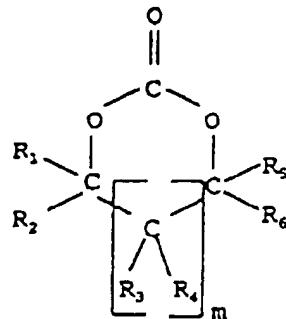
10 4. Elektrolytsystem nach Anspruch 1 oder 2, dadurch **gekennzeichnet**, daß es zusätzlich zu dem Ethylenkarbonat und dem γ -Valerolacton ein oder mehrere der folgenden Lösungsmittel enthält:

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(a) alicyclische Carbonate der folgenden allgemeinen Formel:

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worin R_1 , R_2 , R_3 , R_4 , R_5 und R_6 jeweils unabhängig voneinander für Wasserstoff oder C_1 - C_2 -Alkylgruppen stehen und m eine ganze Zahl von 0 oder 1 ist, mit der Maßgabe, daß wenn m gleich 0 ist, mindestens eine der Gruppen R_1 , R_2 , R_5 und R_6 sich von Wasserstoff unterscheidet, vorzugsweise Propylencarbonat;

30

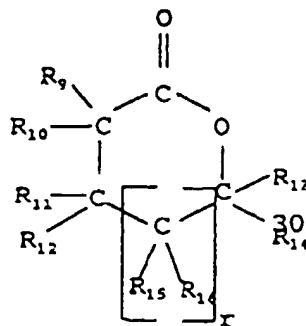
(b) aliphatische Carbonate der allgemeinen Formel $R_7[OC(O)]_pOR_8$, worin R_7 und R_8 unabhängig voneinander für C_1 - C_4 -Alkylgruppen stehen und p eine ganze Zahl von 1 oder 2 ist, vorzugsweise Dimethylcarbonat und/oder Diethylcarbonat;

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(c) Lactone in Form von cyclischen Estern der allgemeinen Formel:

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worin R_9 , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} und R_{16} jeweils unabhängig für Wasserstoff oder C_1 - C_2 -Alkylgruppen stehen und r eine ganze Zahl ist, die 0 oder 1 gleich ist, mit der Maßgabe, daß der Wert von r und die Natur der Substituenten so ausgewählt werden, daß γ -Valerolacton von der Definition ausgeschlossen ist, vorzugsweise γ -Butyrolacton;

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(d) Ester der Formel $R_{17}[C(O)]OR_{18}[OR_{19}]_t$, worin R_{17} , R_{18} und R_{19} jeweils unabhängig für Wasserstoff oder C_1 - C_2 -Alkylgruppen stehen, und t eine ganze Zahl von 0 bis 2 ist, vorzugsweise ein Acetat, mehr bevorzugt (2-Methoxyethyl)acetat und/oder Ethylacetat;

(e) Glyme der allgemeinen Formel $R_{20}O(R_{21}O)_nR_{22}$, worin R_{20} und R_{22} unabhängig für C_{1-2} -Alkylgruppen stehen, R_{21} für $-(CR_{23}R_{24}CR_{25}R_{26})-$ steht, wobei R_{23} , R_{24} , R_{25} und R_{26} unabhängig voneinander jeweils für Wasserstoff oder C_1-C_4 -Alkylgruppen stehen, und n eine ganze Zahl von 2 bis 6, vorzugsweise 3, ist, R_{20} und R_{22} vorzugsweise Methylgruppen sind, R_{23} , R_{24} , R_{25} und R_{26} vorzugsweise Wasserstoff oder C_1-C_2 -Alkylgruppen, mehr bevorzugt Wasserstoff, sind.

5 5. Elektrolytsystem nach einem der vorstehenden Ansprüche, dadurch **gekennzeichnet**, daß das Salz ein Alkalosalz oder ein quaternäres Ammoniumsalz von ClO_4^- , $CF_3SO_3^-$, AsF_6^- , PF_6^- oder BF_4^- , oder ein beliebiges Gemisch von solchen Alkali- oder Ammoniumsalzen, vorzugsweise $LiAsF_6$, $LiPF_6$, $N(Et)_4PF_6$ oder $N(Bu)_4PF_6$ oder beliebige Gemische davon, ist.

10 6. Elektrolytsystem nach einem der vorstehenden Ansprüche, dadurch **gekennzeichnet**, daß es ein vernetztes oder nichtvernetztes, vorzugsweise nichtvernetztes, Polymeres enthält, das durch UV- oder hitzeinduzierte Polymerisation von Monomeren oder Oligomeren, enthaltend ein oder mehrere polymerisierbare funktionelle Gruppen, hergestellt ist, wobei das Polymere mehr bevorzugt ein nichtvernetzbares Polyester, Polyurethan, Polyether oder Polyacrylat ist.

15 7. Elektrolytsystem nach Anspruch 6, dadurch **gekennzeichnet**, daß das Polymere durch hitzeinduzierte Polymerisation bei einer Temperatur von niedriger als $70^\circ C$ hergestellt worden ist.

20 8. Elektrolytsystem nach einem der vorstehenden Ansprüche, dadurch **gekennzeichnet**, daß das System in einem Separator eingegrenzt ist, der, aus einer porösen Struktur hergestellt, aus einem Polymeren, vorzugsweise Polyethylen, Polypropylen, Polycarbonat oder Cellulose, besteht.

25 9. Elektrolytsystem nach Anspruch 8, dadurch **gekennzeichnet**, daß der Separator eine gewebte oder nichtgewebte Struktur mit einer Porengröße im Bereich von $10 \times 10 \text{ nm}$ bis $1 \times 1 \text{ mm}$ ist.

30 10. Elektrolytsystem nach einem der Ansprüche 8 und 9, dadurch **gekennzeichnet**, daß der Separator eine Dicke von $10-100 \mu\text{m}$, vorzugsweise $10-25 \mu\text{m}$ hat.

11. Elektrolytsystem nach einem der vorstehenden Ansprüche, dadurch **gekennzeichnet**, daß das Alkali- oder Ammoniumsalz in einer Konzentration von $0,01 \text{ M}$ bis $2,5 \text{ M}$, vorzugsweise $0,1 \text{ M}$ bis $1,5 \text{ M}$, vorhanden ist.

35 12. Elektrolytsystem nach einem der vorstehenden Ansprüche, dadurch **gekennzeichnet**, daß das Polymere in einer Menge entsprechend 3 bis 95 Gew.-%, vorzugsweise 5 bis 70 Gew.-%, mehr bevorzugt 5 bis 40 Gew.-%, noch mehr bevorzugt 15 bis 40 Gew.-%, bezogen auf das Gesamtgewicht des Elektrolytsystems, vorhanden ist.

13. Verfahren zur Herstellung eines Elektrolytsystems nach einem der vorstehenden Ansprüche, umfassend Vermischung der Lösungsmittel, Auflösung der Alkali- oder Ammoniumsalze in dem Lösungsmittelgemisch und gegebenenfalls Zusetzung eines Verdickungsmittels zu der Lösung.

40 14. Verfahren nach Anspruch 13, dadurch **gekennzeichnet**, daß weiterhin Monomere oder Oligomere, enthaltend ein oder mehrere polymerisierbare funktionelle Gruppen, zugegeben werden, daß ein UV-Photoinitiator oder ein Hitzeinitiator zugesetzt wird und daß gegebenenfalls das erhaltene Gemisch in einen Separator eingearbeitet wird und die Monomeren oder Oligomeren durch UV oder durch Hitze gehärtet werden.

45 15. Verwendung des Elektrolytsystems nach den Ansprüchen 1 bis 12 in einer Batterie, einem Kondensator und/oder einem elektrochromen Display.

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Revendications

55 1. Système électrolytique non aqueux destiné à être utilisé dans des batteries, des condensateurs ou des affichages à électrochromes, ledit système étant essentiellement constitué de :

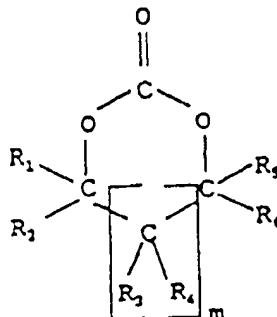
- un sel alcalin ou d'ammonium
- un mélange de solvants, et éventuellement
- un polymère,

caractérisé en ce que le mélange de solvants comprend au moins 50 % en mole d'un mélange de carbonate d'éthylène et de γ -valérolactone, contenant éventuellement un ou plusieurs solvants supplémentaires choisis parmi d'autres carbonates organiques, d'autres lactones, esters et glymes, ledit système étant éventuellement confiné dans un séparateur.

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2. Système électrolytique selon la revendication 1, dans lequel le carbonate d'éthylène et la γ -valérolactone sont présents dans le mélange de solvants dans un rapport molaire relatif allant de 20/80 à 80/20.
- 10 3. Système électrolytique selon la revendication 1 ou 2, dans lequel le mélange de solvants se compose d'au moins 90 % de carbonate d'éthylène et de γ -valérolactone, de préférence, se compose essentiellement de carbonate d'éthylène et de γ -valérolactone seulement.
- 15 4. Système électrolytique selon la revendication 1 ou 2, qui, en plus du carbonate d'éthylène et de la γ -valérolactone, comprend un ou plusieurs des solvants suivants :

15 (a) des carbonates alicycliques représentés par la formule générale suivante :

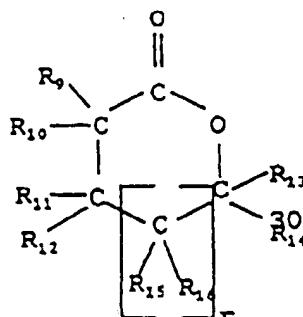


25 dans laquelle chaque R₁, R₂, R₃, R₄, R₅ et R₆ représente indépendamment un atome d'hydrogène ou des groupes alkyle en C₁₋₂, et m est un nombre entier égal à 0 ou 1, à la condition que lorsque m est égal à 0, au moins un parmi R₁, R₂, R₅ et R₆ est différent d'un atome d'hydrogène, de préférence du carbonate de propylène ;

30 (b) des carbonates aliphatiques représentés par la formule générale R₇[OC(O)]_pOR₈, dans laquelle R₇ et R₈ représentent indépendamment des groupes alkyle en C₁₋₄, et p est un nombre entier égal à 1 ou 2, de préférence du carbonate de diméthyle et/ou du carbonate de diéthyle ;

35 (c) des lactones sous la forme d'esters cycliques représentés par la formule générale :

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55 dans laquelle chaque R₉, R₁₀, R₁₁, R₁₂, R₁₃, R₁₄, R₁₅ et R₁₆ représente indépendamment un atome d'hydrogène ou des groupes alkyle en C₁₋₂, et r est un nombre entier égal à 0 ou 1, à condition que la valeur de r et la nature des substituants soient choisies de façon à exclure la γ -valérolactone de la définition, de préférence la γ -butyrolactone ;

(d) des esters représentés par la formule $R_{17}[C(O)]OR_{18}[OR_{19}]_t$, dans laquelle chacun des R_{17} , R_{19} et R_{19} représente indépendamment un atome d'hydrogène ou un groupe alkyle en C_{1-2} , et t est un nombre entier compris entre 0 et 2, de préférence un acétate, mieux encore l'acétate de 2-méthoxyéthyle et/ou l'acétate d'éthyle ;

(e) des glymes représentés par la formule générale $R_{20}O(R_{21}O)_nR_{22}$, dans laquelle R_{20} et R_{22} représentent indépendamment des groupes alkyle en C_{1-2} , R_{21} représente $-(CR_{23}R_{24}CR_{25}R_{26})$, où R_{23} , R_{24} , R_{25} et R_{26} représentent chacun indépendamment un atome d'hydrogène ou des groupes alkyle en C_{1-4} , et n est un nombre entier de 2 à 6, de préférence 3, R_{20} et R_{22} représentant de préférence des groupes méthyle, R_{23} , R_{24} , R_{25} et R_{26} représentant de préférence un atome d'hydrogène ou des groupes alkyle en C_{1-2} , mieux encore un atome d'hydrogène.

5. Système électrolytique selon l'une quelconque des revendications précédentes, dans lequel ledit sel est un sel alcalin ou un sel d'ammonium quaternaire de ClO_4^- , $CF_3SO_3^-$, ASF_6^- , PF_6^- ou BF_4^- , ou un mélange quelconque de ces sels alcalins ou d'ammonium, de préférence, $LiAsF_6$, $LiPF_6$, $N(Et)_4PF_6$ ou $N(Bu)_4PF_6$ ou des mélanges quelconques de ceux-ci.

10. Système électrolytique selon l'une quelconque des revendications précédentes comprenant un polymère réticulé ou non réticulé, de préférence non réticulé, produit par polymérisation aux U.V. ou à la chaleur de monomères ou d'oligomères contenant un ou plusieurs groupes fonctionnels polymérisables, ledit polymère étant mieux encore un polyester, un polyuréthane, un polyéther ou un polyacrylate non réticulable.

15. Système électrolytique selon la revendication 6, dans lequel le polymère est produit par polymérisation induite par la chaleur à une température inférieure à 70°C.

20. Système électrolytique selon l'une quelconque des revendications précédentes, ledit système étant confiné dans un séparateur constitué d'une structure poreuse fabriquée dans un polymère, de préférence du polyéthylène, du polypropylène, du polycarbonate ou de la cellulose.

25. Système électrolytique selon la revendication 8, dans lequel ledit séparateur est fait dans une structure tissée ou non tissée ayant une taille de pores comprise dans l'intervalle allant de 10 x 10 nm à 1 x 1 mm.

30. Système électrolytique selon l'une quelconque des revendications 8 et 9, dans lequel ledit séparateur a une épaisseur de 10-100 μm , de préférence de 10-25 μm .

35. Système électrolytique selon l'une quelconque des revendications précédentes, dans lequel le sel alcalin ou d'ammonium est présent en une concentration allant de 0,01 M à 2,5 M, de préférence de 0,1 M à 1,5 M.

40. Système électrolytique selon l'une quelconque des revendications précédentes, dans lequel le polymère est présent en une quantité correspondant à 3 % à 95 % en poids, de préférence 5 % à 70 % en poids, mieux encore 5 % à 40 % en poids, et mieux encore 15 % à 40 % en poids, par rapport au poids total du système électrolytique.

45. Méthode pour la préparation d'un système électrolytique selon l'une quelconque des revendications précédentes, comprenant les étapes consistant à mélanger les solvants, à dissoudre les sels alcalins ou d'ammonium dans le mélange de solvants et à ajouter éventuellement un agent épaisseur à la solution.

50. Méthode selon la revendication 13, comprenant en outre l'addition de monomères ou d'oligomères contenant un ou plusieurs groupes fonctionnels polymérisables, l'addition d'un photoamorceur aux U.V., ou d'un amorceur à la chaleur, éventuellement l'incorporation du mélange obtenu dans un séparateur et le durcissement par les U.V. ou la chaleur des monomères ou des oligomères.

55. Utilisation d'un système électrolytique selon les revendications 1 à 12 dans une batterie, un condensateur et/ou dans un affichage à électrochromes.